

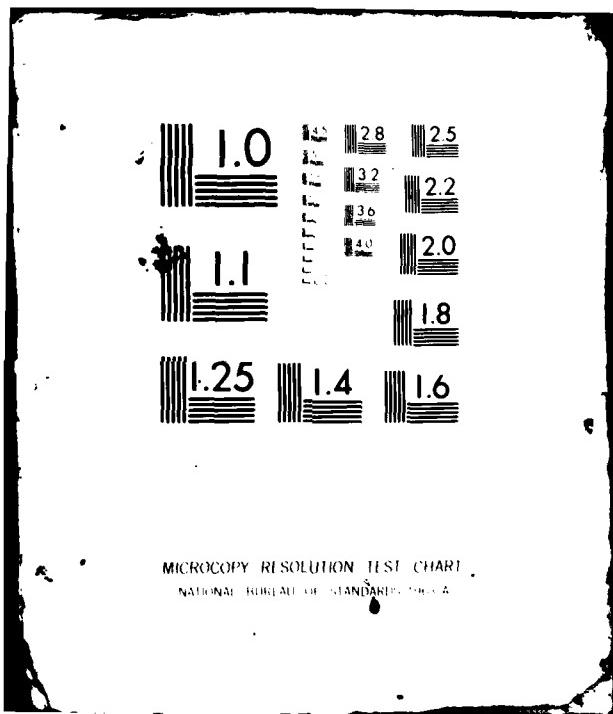
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ELECTROCHEMICAL ISOMERIZATION OF CIS-(CH)_X TO TRANS-(CH)_X. (U)
JAN 82 T CHUNG, A G FELDBLUM, A G MACDIARMID N00014-81-K-0648
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Summary

Electrochemical isomerization of films of cis-(CH)_x may be accomplished conveniently by first n-doping the (CH)_x with (Bu₄N)⁺ to the metallic regime or p-doping the (CH)_x with (ClO₄)⁻ to the metallic regime followed in each case by electrochemical undoping to yield pure trans-(CH)_x.

Cis-(CH)_x is isomerized to the more thermodynamically stable trans isomer by heating briefly at 150-200°C.¹ Isomerization also takes place during chemical p- or n-doping and/or "undoping", i.e., compensation, but no agreement has been reached as to when isomerization commences or when it is complete. Furthermore, no pure trans-(CH)_x has been produced by chemical isomerization methods since the final product has always been obtained in the doped state² or partly hydrogenated state.² We have shown previously, using electrical conductivity measurements, that (CH)_x may be p- or n-doped electrochemically to the metallic state.³ A conductivity in the approximate range 50-1000 ohm⁻¹ cm⁻¹ at room temperature was used to indicate that the metallic state had been reached. The present study was performed in order to (i) show that isomerization can be attained by electrochemical doping of cis-(CH)_x followed by its electrochemical undoping to parent trans-(CH)_x; (ii) confirm the electrochemical conversion of (CH)_x to the p- or n-doped metallic state by physical measurements other than electrical conductivity; and (iii) to show that electrochemical and also chemical isomerization of cis-(CH)_x to trans-(CH)_x take place via the intermediate formation of chemically similar doped (CH)_x species.

I. Electrochemical Studies

A very important characteristic feature of electrochemical doping is that application of a given potential to a (CH)_x electrode results in a given level of p- or n-doping when equilibrium or near equilibrium conditions are established. The doped (CH)_x can be undoped subsequently by applying the potential characteristic of parent (CH)_x in a given electrolyte.

A Pyrex electrochemical cell was constructed so that the visible/near

ir spectrum of the $(CH)_x$ could be recorded throughout the electrochemical doping and/or undoping processes. A thin cis-rich $(CH)_x$ film was polymerized on a conductive glass electrode which was immersed in the electrolyte solution. When trans-($CH)_x$ was required, the cis film was thermally isomerized in situ before adding the electrolyte. A lithium wire served as the other electrode. The "blank" spectrum of the cell and electrolyte was recorded, stored in a computer, and electronically subtracted from the spectra of the doped and undoped $(CH)_x$ as required. All potentials given are with respect to a lithium metal reference electrode. It has been found from studies of the open circuit voltage, V_{oc} (the voltage measured when no current is flowing) that a threshold exists below which charge is not injected. Thus voltages in the range between about 2.2-2.8 V are characteristic of parent $(CH)_x$.

(i) Electrochemical p-doping of Trans-($CH)_x$ with $(ClO_4)^-$

The trans-($CH)_x$ electrode was attached to the positive terminal of a constant voltage power supply. A 1.0M solution of $LiClO_4$ in propylene carbonate was used as the electrolyte. $V_{applied}$ potentials (measured as current was passing) were applied for ca. 30 minute periods during which time the current fell from ca. 20 μ A to ca. 0.2 μ A. Spectra were recorded at the following values of $V_{applied}$ (dopant levels given in parentheses); 3.46V (1.2%), 3.57V (2.5%), 3.64V (3.7%), 3.73V (6.8%). Doping levels were obtained from V_{oc} versus charge data relating V_{oc} values to percent doping.⁴ The error introduced will be small since $V_{applied}$ and V_{oc} values will not differ greatly under the quasi-equilibrium conditions at the end of the 30 minute periods. As doping proceeded, the intensity of the trans peak at 2.0 ev decreased continually while at the same time the mid-gap soliton transition⁵ at 0.7-0.8 ev increased. At 3.73V, i.e., at a composition corresponding to $[CH(ClO_4)_{0.068}]_x$ both these peaks had been replaced by the free carrier spectrum characteristic of the metallic state identical to that found in highly chemically p-doped⁶ trans-($CH)_x$.

(ii) Electrochemical Isomerization of Cis-(CH)_x to Trans-(CH)_x

Electrochemical isomerization was carried out by either n-doping or p-doping cis-(CH)_x* (ca. 85% cis isomer) to the metallic regime, followed by electrochemical undoping.

N-doping was accomplished using a similar apparatus to that discussed in (i) except that the two electrodes were separated by a fine glass frit. The electrolyte was a 1.0M solution of $(Bu_4N)(ClO_4)$ in THF. Electrochemical n-doping occurs spontaneously; the constant voltage power supply was used simply to maintain the voltage applied to the cis-(CH)_x at a given pre-selected fixed value which would result in a given level of doping (or undoping) when the final doping current had fallen to 1-2% of the initial value. Figure 1, spectrum 1, is that of the parent cis isomer. Spectra 2-5 were recorded at V_{applied} values of 1.50V (~1%), 1.35V (~3%), 1.30V (~5%) and 1.25V (~8%), respectively, to give n-doped material of composition $(Bu_4N)_y^{+}CH_x$ (y =mole fraction of dopant, Bu_4N^+).⁷ As can be seen from spectra 1-5, the peaks characteristic of cis-(CH)_x at 2.1 and 2.3 ev decreased continually on doping, and the soliton mid-gap peak at (0.7-0.8 ev) characteristic of doped trans-(CH)_x appeared and increased with doping. At 1.25V the spectrum characteristic of the metallic state, essentially identical to that observed in highly chemically n-doped (with Na^+) trans-(CH)_x⁸ was obtained. The spectrum was also identical to that obtained in (i) by the electrochemical p-doping of trans-(CH)_x. On applying potentials of 2.0V and 2.8V, spectra 6 and 7, respectively, were obtained, the latter being essentially identical to that of pure trans-(CH)_x formed by thermal isomerization of cis-(CH)_x. These results are consistent with isomerization occurring upon doping; the pure parent trans isomer is then obtained upon undoping.

In a further series of experiments, ca. 85% cis-(CH)_x was doped electrochemically with $(Bu_4N)^+$ to ca. 1% ($V_{\text{applied}} = 1.50V$) and was then undoped (at 2.7V) to parent (CH)_x. A small increase in the peak characteristic of the trans isomer

*It is convenient to refer to "doping of cis-(CH)_x"; however, we show in these studies that as soon as cis-(CH)_x is "doped" it converts spontaneously to doped trans-(CH)_x.

and a corresponding decrease in the peaks of the *cis* isomer were observed in the visible/near ir absorption spectrum. This doping-undoping cycle was repeated seven times, the extent of isomerization decreasing after each of the first three cycles. After the fourth cycle, no further isomerization occurred. In a related experiment, a *cis*-rich sample was first doped to a concentration y_1 , then undoped to parent neutral $(CH)_x$. On subsequent doping to $y_2 < y_1$, no additional isomerization occurred. These results show that doping of the *trans* isomer occurs preferentially to the reaction of the *cis* isomer with the dopant. It should be noted that that portion of the *cis* isomer which had undergone reaction with the dopant is apparently converted to the *trans* isomer at some stage during the doping-undoping cycle. Thus subsequent undoping and re-doping to the same level re-dopes only that portion of the material which was already *trans*.

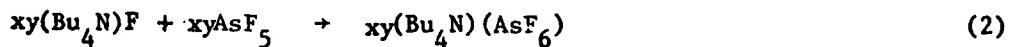
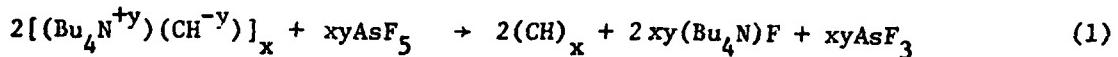
In another study, a free standing film of *cis*-rich $(CH)_x$, to which a platinum wire was affixed, was n-doped to composition $[(Bu_4N)_0.03(CH)]_x$ by placing it in the electrolyte and short-circuiting it to a lithium wire also in the electrolyte. Spontaneous electrochemical doping occurred. It exhibited a conductivity in the metallic regime ($25 \text{ ohm}^{-1} \text{cm}^{-1}$). Its thermoelectric power at room temperature ($-43.5 \mu\text{V/K}$) was characteristic of an n-type metal. Moreover, in the heavily doped regime the thermoelectric power decreased linearly with temperature, consistent with metallic behavior.

P-doping of *cis*- $(CH)_x$ (ca. 85% *cis* isomer) was accomplished at $V_{\text{applied}} = 3.83\text{V}$ in the same apparatus and in the same manner as in (i). A spectrum identical to that observed by either p-doping *trans*- $(CH)_x$ or n-doping *cis*- $(CH)_x$ (Figure 1, Spectrum 5) was obtained. The sample was subsequently undoped by setting the applied voltage to 2.0V. The spectrum then showed no evidence of *cis*- $(CH)_x$ peaks and consisted only of the peak characteristic of undoped *trans*- $(CH)_x$.

(iii) Electrochemical Doping/Chemical Undoping Induced Isomerization of *Cis*- $(CH)_x$ to *Trans*- $(CH)_x$

Cis - $(CH)_x$ film (ca. 85% *cis* isomer; 0.01 mm thick) was polymerized on

a platinum grid and was n-doped with $(Bu_4N)^+$ in a similar manner to that employed for the preparation of the sample used in the thermoelectric power studies. The film was completely opaque in the ir region, consistent with its being doped to the metallic state. It was then undoped in the ir cell by exposing it to ~0.1 Torr of AsF_5 vapor until the characteristic soliton peak at 1380 cm^{-1} ⁹ disappeared completely to yield a spectrum characteristic of undoped trans-(CH)_x containing $(Bu_4N)^+(AsF_6)^-$ formed according to equations (1) and (2):



II. Chemical Isomerization

Cis-(CH)_x was chemically doped with Na^+ using sodium naphthalide solution in THF. Doping and washing were carried out as previously described⁸ for epr studies of Na-doped trans-(CH)_x except that the epr tube was replaced by a rectangular Pyrex cell on the inside walls of which a thin film of cis-(CH)_x had been polymerized. Successive doping, washing and visible/near ir spectral studies were carried out in situ. As doping proceeded, the intensity of the characteristic cis peaks at 2.1 ev and 2.3 ev decreased and the soliton mid-gap peak at 0.8 ev appeared and increased in intensity. Finally, the only absorption present was that characteristic of the free carrier metallic state. The $[Na_y(CH)]_x$ was then undoped with 0.1 Torr of AsF_5 vapor. As this compensation reaction proceeded, the 0.8 ev peak again appeared and then decreased in intensity while at the same time, the 2.0 ev peak characteristic of trans-(CH)_x appeared and grew in intensity. The final spectrum obtained showed only the presence of the trans-(CH)_x absorption indicating complete isomerization.

A similar experiment was carried out except that undoping was accomplished by the use of iodine vapor and that the doping and undoping was constantly moni-

tored by observing changes in the ir spectrum. The NaI formed in the reaction with iodine was removed by washing with water. The ir spectrum of the resulting film showed it consisted of pure trans-(CH)_x.

All methods of isomerization, including thermal isomerization, give trans-(CH)_x containing approximately the same number of unpaired spins and an epr signal of the same g value and line width.

Cis/trans isomerization of (CH)_x has been shown to occur in these studies as proceeding via a doping-undoping cycle involving the metallic state of (CH)_x regardless of whether the cycles are completely electrochemical in nature, completely chemical or partly electrochemical and partly chemical. The results imply that isomerization occurs continuously during the doping step.

Acknowledgement

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Figure 1: Visible-near ir absorption spectral changes during the cis-trans isomerization of $(CH)_x$ film by electrochemical n-type $(Bu_4N)^+$ doping.

- (1) $V_{oc} = 2.7 \text{ V}$; $(cis-(CH)_x)$
- (2) $V_{applied} = 1.5 \text{ V}$
- (3) $V_{applied} = 1.35 \text{ V}$
- (4) $V_{applied} = 1.3 \text{ V}$
- (5) $V_{applied} = 1.25 \text{ V}$
- (6) $V_{applied} = 2.0 \text{ V}$
- (7) $V_{applied} = 2.8 \text{ V}$

